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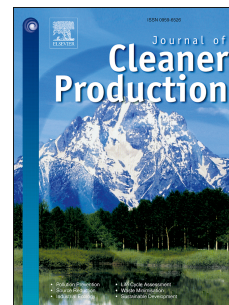
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Life cycle assessment of nanoadsorbents at early stage technological development

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Abstract

Increasing pressure to the environment due to human activities manifests the necessity of applying new approaches to determine the environmental impact of a new product before scale-up. Nanoadsorbents as an emerging product and a special application of nanomaterial play an important role in the control and removal of environmental pollutants. This application is still an emerging technology at the early stages of development. Hence, the heart of this study enables an environmental assessment of nanoadsorbents as an emerging product. In addition, the environmental impacts of synthesized adsorbents including cumulative energy demand, climate change, water use, human toxicity, and ecotoxicity are investigated by a stepwise procedure during their synthesis processes, regarding their potential to remove mercury from polluted water. Accordingly, characterization results showed that although the process of the functionalization of nanoadsorbents leads to the increase of the adsorption capacity of nanoadsorbents, it is also paired with a significant enhancement of negative environmental impacts. The results of t-test comparing the cradle-to-use life cycle impacts of studied impact categories for 1 kg Hg removal between MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ estimated approximately 37, 34, 40, 31, and 26% more for climate change, water use, cumulative energy demand, human toxicity, and ecotoxicity, respectively for the latter. Hence, according to the results, $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ revealed the larger environmental impacts from the same functional unit, 1 kg Hg removal, compared with MGO-NH-SH. Finally, not only does this study represents the LCA of two different kinds of mercury adsorbents, but it also provides a guideline for determining the environmental impacts of similar nanoadsorbents.

Keywords: LCA, Nanoadsorbents, Mercury, Removal, Prospective approach

1. Introduction

The presence of various pollutants (e.g. toxic metal ions) in water and wastewater causes serious environmental concerns (Cui et al., 2015b; Guo et al., 2014a). One of these is mercury which is a hazardous and pervasive environmental pollutant (Cui et al., 2015a; Hadavifar et al., 2014). This is for example seen in Japan where many people in the past decades have been adversely affected and thousands of people have died of Minamata disease, caused by a chemical plant's release of wastewater containing elevated levels of mercury pollution (Graeme and Pollack, 1998; Igata, 1994). Elevated mercury levels in the environment is caused by a variety of anthropogenic sources, including coal combustion in power plants, chlor-alkali production, alumina production from bauxite, oil refining, and mercury emissions (Diagboya et al., 2015; Hadavifar et al., 2014).

In aqueous systems, mercury can be present in one or more different oxidation states: Hg^0 (metallic), Hg_2^{2+} (mercurous), and Hg^{2+} (mercuric). The solubility of different compounds of mercury differ greatly in water. Solubility in water increases in the following order: elemental mercury < mercurous chloride < methylmercury chloride < mercuric chloride (Boening, 2000; O'Driscoll et al., 2005; S. Zhang et al., 2013). Among mercury species, it is largely Hg^{2+} that can react with various organic compounds in water and sediment by biotic reactions mediated by sulfur-reducing bacteria, and abiotic reactions mediated by sunlight photolysis, resulting in conversion into organic mercury compounds, such as methylmercury (MeHg). MeHg is known as a bioaccumulative and toxic substance for humans and the environment. For example, when ingested into the human body, it undergoes oxidation and reduction reactions, which transforms it into bivalent inorganic mercury. When MeHg undergoes these reactions, oxygen radicals are released, causing extensive injury to cells by activating the chain of lipid peroxidation in the cell membrane. In addition, it has been confirmed that MeHg has high fat solubility; hence, it is

especially toxic to the organs of the body that have a high fat content (Boening, 2000; Graeme and Pollack, 1998; Hadavifar et al., 2014; O'Driscoll et al., 2005; Shen et al., 2014; Starvin and Rao, 2004; S. Zhang et al., 2013). Therefore, mercury (II) was selected in this study to examine its removal from wastewater and polluted water.

Methods including reverse osmosis, biological treatments, chemical precipitation, ion exchange, coagulation, electrochemical treatment, and adsorption have been utilized to remove metal ions and other pollutants from water before discharge into the environment (Hadavifar et al., 2016; Oehmen et al., 2014; H. Wang et al., 2011). Most of these methods are inefficient and not suitable considering environment and economy, particularly for wastewater with only trace amounts of mercury. Hence, developing different efficient technologies for removing Hg(II) and other pollutants is essential. With increasingly strict environmental regulations on the release of pollutants and growing demands for clean water with the lowest levels of pollutants, extensive attention by researchers has been paid to producing nanoadsorbents for removing pollutants from water and wastewater (Li et al., 2011; Pan et al., 2012) and the use of nanoadsorbents to remove mercury (II) from water and wastewater has received considerable attention in chemical engineering and environmental science (Cui et al., 2015b; Hadavifar et al., 2016; Lopes et al., 2014; S. Zhang et al., 2013). To increase the adsorption rate and selectivity of adsorbents, they are organized into different functional groups (e.g. amine, thiol, ...) (Ke et al., 2011; Li et al., 2011; Ma et al., 2016; Monier, 2012; Pan et al., 2012). Although nanoadsorbents are still in early stages of technological development, further development of them is expected to soon advance. However, each new material or development has its own negative and positive environmental impacts in production, use, and disposal. For example, it is illogical to use a nanoadsorbent for pollutant removal if its production demands large amounts of energy and water, and other

pollutants are emitted into the air, soil, and water contributing to e.g. climate change, ecotoxicity, and human toxicity.

As we know, each development starts with an idea, leads to research and lab work, progresses to publication of scientific papers, is followed by semi-industrial pilots, and finally, industrial development will occur. Accordingly, assessing the environmental impacts already during the initial stages of development can help identify potential trade-offs and possibly leads to development of more sustainable nanoadsorbents with fewer negative environmental impacts. Life cycle assessment (LCA) of different nanomaterials (e.g. nanoadsorbents) enables a prospective approach to assessment of environmental impacts of products and their uses at early stages of technological development (Arvidsson et al., 2014; Gavankar et al., 2015; Hirschler and Walser, 2012). Hence, assessing the environmental impacts of each product at the first stages of development is essential for identification and understanding of negative environmental impacts at different stages of production, use, and disposal, and avoidance of these by changing or modifying these stages. Unfortunately, environmental impacts of nanoadsorbents' production are hardly ever found in the literature. Hence, this study investigates for the first time the environmental impacts of nanoadsorbents' production and functionalization.

We study the environmental impacts in the production and use stages of two nanoadsorbents with graphene-based and Fe_3O_4 -based composites, which function with a similar thiol group for Hg(II) removal. Graphene-based and Fe_3O_4 -based composite nanoadsorbents are recognized for their high efficiency in removing environmental pollutants (Ai et al., 2011; Cui et al., 2015a; Dubey et al., 2015; Guo et al., 2014b; Liu et al., 2011). Graphene-based nanoadsorbents, especially if they possess magnetic properties, and Fe_3O_4 -based nanoadsorbents, with their

magnetic properties, can easily be separated from water and wastewater solution, and can be repeatedly reused (Ai et al., 2011; C. Wang et al., 2011; Wang et al., 2015; Yu et al., 2015).

2. Materials and methods

2.1. Goal and scope of the study

This study compares the environmental impacts of the functionalization of the GO-based and Fe_3O_4 -based composites for the removal of 1 kg Hg(II) from polluted water. Nanoadsorbents are in early stages of technological development in the laboratory; therefore, the investigation of environmental impacts in their production and use stages is still highly uncertain. Hence, sensitivity analysis will be employed to determine these uncertainties for scale-up production.

LCA of nanostructure products and their applications is relatively new (Healy et al., 2008; Kim and Fthenakis, 2013; Klöpffer et al., 2007). This study is an LCA of nanoadsorbents as a special application of nanomaterials for the removal of pollutants from the environment. The LCA is attributional, with prospective analysis of emerging and immature products, similar to the studies by Walser et al. (2011), Healy et al. (2008), and Arvidsson et al. (2015 and 2014) albeit with different system boundaries. As mentioned above, the main goal of the study is to assess cradle-to-use life cycle impacts of thiol-functionalized magnetic graphene oxide, and superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$, for application in water and wastewater treatment. Since the produced adsorbents have different adsorption capacities, the functional unit was determined to be 1 kg Hg removal of pollutant water. In environmental evaluations, total adsorption capacity for both nanoadsorbents was calculated based on an adsorption-desorption cycle of more than 90% (Cui et al., 2015b; Hadavifar et al., 2014). Table 1 of Supporting Information (SI) presents the adsorption capacities and number of adsorption-desorption cycles (more than 90%) for each

adsorbent. Fig. 1 shows the scope and system boundaries of the stepwise procedure of both synthesized adsorbents that were functionalized with a similar thiol functional group (N-acetylcysteine).

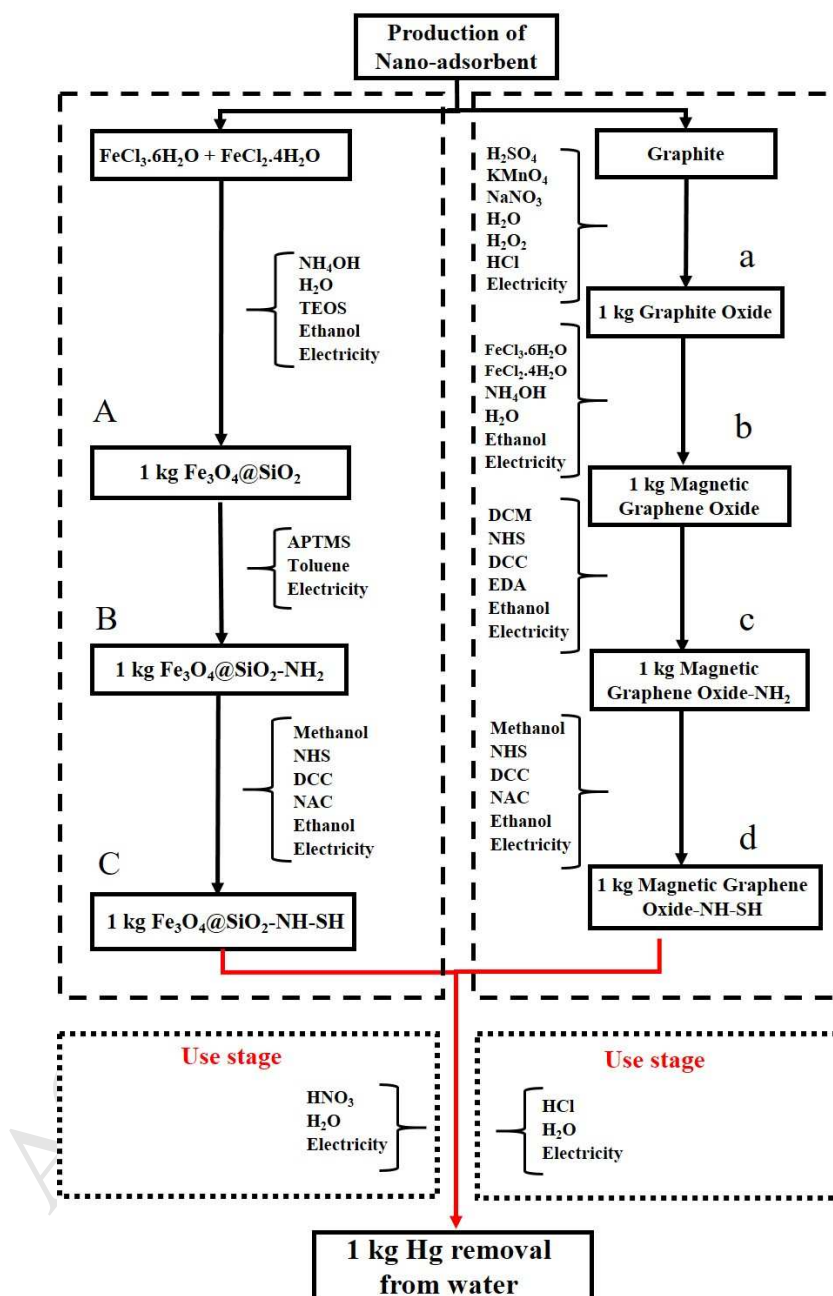


Fig. 1. Flowchart describing the cradle-to-use life cycle of adsorbents production, thiol-functionalized magnetic graphene oxide, and superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$, for 1 kg Hg removal of polluted water, respectively.

2.2. Life cycle inventory

Life cycle inventory (LCI) analysis is the second phase in an LCA study. The LCI is the data collection portion of all recognized inputs/outputs to or from the system boundary (Rajaeifar et al., 2016). On this basis, our laboratory experiments provided the process data for assessing cradle-to-use life cycle impacts of the produced adsorbents. Sections 1 and 2 of SI detail the synthesis of both adsorbents. Inputs and outputs in each stage were converted to the scale of 1 kg Hg(II) removal. Tables 1 and 2 present the life cycle inventory for generating final products, including MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}-\text{SH}$, based on 1 kg Hg(II) removal. Tables 2 and 3 in SI display the LCI data for producing GO, MGO, MGO-NH₂, and Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}_2$ for 1 kg Hg(II) removal. The Ecoinvent 3.2. database was the source of inventory data for all input materials and energy in this study; however, there were no data for APTMS, DCC, NHS, or N-AC in this database or elsewhere. Consequently, hexamethyldisilazane from the ecoinvent database was used as proxy data for APTMS. Lacking production data for DCC, NHS, and N-AC, their production was modeled in detail based on the stoichiometric formula (see Section 3 in SI). Electricity was the predominant source of energy used in the lab experiments, mainly for heating and cooling. The inventory of electricity use was gained from the Ecoinvent 3.2. database, based on the electricity mix produced in Iran.

Table 1

The synthesis process and inventory data of MGO-NH-SH for 1 kg Hg removal from pollutant water

Production stage			
Synthesis process for graphite oxide		CAS Number	Amount used
<i>Input</i>	Graphite	7782-42-5	0.25 kg
	NaNO ₃	7631-99-4	0.17 kg
	H ₂ SO ₄	7664-93-9	9.97 L
	H ₂ O ₂	7722-84-1	2.49 L
	HCl	7647-01-0	11.22 L
	Water		1520 L
	Electricity		382.93 kWh
<i>Output</i>	Graphite oxide		0.225 kg
Synthesis process for MGO	Graphite oxide		0.225 kg
<i>Input</i>	FeCl ₃ .6H ₂ O	10025-77-1	1.21 kg
	FeCl ₂ .4H ₂ O	13478-10-9	0.44 kg
	NH ₄ OH	1336-21-6	33.67 L
	Ethanol	64-17-5	56.13 L
	Water		1347.28 L
	Electricity		1670.63 kWh
<i>Output</i>	MGO		0.73 kg
Synthesis process for MGO-NH ₂	MGO		0.73
<i>Input</i>	EDA	107-15-3	1.82 L
	NHS	6066-82-6	0.25 kg
	DCC	538-75-0	0.42 kg
	Ethanol	64-17-5	729.57 L
	Electricity		1167.32 kWh
<i>Output</i>	MGO-NH ₂		0.79 kg
Synthesis process for MGO-NH-SH	MGO-NH ₂		0.79 kg
<i>Input</i>	Acetylcysteine	616-91-1	0.33 kg
	Methanol	67-56-1	198.85 L
	NHS	6066-82-6	0.28 kg
	DCC	538-75-0	0.45 kg
	Ethanol	64-17-5	795.26 L
	Electricity		1273.80 kWh
<i>Output</i>	MGO-NH-SH		0.83 kg
Use stage			
<i>Input</i>	MGO-NH-SH		0.83 kg
	HCl	7647-01-0	13.18 L
	Water		236 L
	Electricity		263.54 kWh
<i>Output</i>	Hg(II) removal		1 kg

Table 2

The synthesis process and inventory data of Fe₃O₄@SiO-NH-SH for 1 kg Hg removal of pollutant water

Production stage			
Synthesis process for Fe ₃ O ₄ @SiO ₂			
<i>Input</i>	FeCl ₃ .6H ₂ O	CAS Number 10025-77-1	Amount used 0.89 kg
	FeCl ₂ .4H ₂ O	13478-10-9	0.43 kg
	NH ₄ OH	1336-21-6	8.60 L
	TEOS	78-10-4	4.30
	Ethanol	64-17-5	275.16 L
	Water		343.95 L
	Electricity		485.92 kWh
<i>Output</i>	Fe ₃ O ₄ @SiO ₂		1.70 kg
Synthesis process for Fe ₃ O ₄ @SiO-NH ₂			
<i>Input</i>	Fe ₃ O ₄ @SiO ₂		1.70 kg
	APTMS	13822-56-5	1.64 L
	Toluene for synthesis	108-88-3	84.34 L
	Toluene for washing	108-88-3	202.43 L
	Electricity		5076.99 kWh
<i>Output</i>	Fe ₃ O ₄ @SiO-NH ₂		1.85 kg
Synthesis process for Fe ₃ O ₄ @SiO-NH-SH			
<i>Input</i>	Fe ₃ O ₄ @SiO-NH ₂		1.85 kg
	Methanol	67-56-1	467.78 L
	NHS	6066-82-6	0.65 kg
	DCC	538-75-0	1.07 kg
	Acetylcysteine	616-91-1	0.76 kg
	Ethanol	64-17-5	1859.15 L
	Electricity		2974.64 kWh
<i>Output</i>	Fe ₃ O ₄ @SiO-NH-SH		1.98 kg
Use stage			
<i>Input</i>	Fe ₃ O ₄ @SiO-NH-SH		1.98 kg
	HNO ₃	7697-37-2	41.58 L
	Water		255.42 L
	Electricity		313.63 kWh
<i>Output</i>	Hg(II) removal		1 kg

2.3. Impact Categories

LCI results may be allocated to environmental matters of concern through impact categories. In this study, four common impact categories (water use, cumulative energy demand, human

toxicity, and ecotoxicity) were investigated similarly to other studies such as Arvidsson et al. (2014). These four impact categories represent to a large extent non-overlapping impact and they are relevant since high volumes and amount of water, acids, and other organic and inorganic materials were used in production processes of both nanoadsorbents. Climate change was studied as one of the more common impact categories in LCA, because the two compared nanoadsorbents use high values of electricity in the production processes. Water use considers the water used during production and use stages of both adsorbents in foreground and background systems. Cumulative energy demand in foreground and background systems in LCA may change fundamentally upon maturation of products. Nevertheless, we investigated total cumulative energy demand (including; all of renewable and non-Renewable energy, and as well direct and indirect), measured in MJ, as a key impact category, which can correlate with other environmental impacts (Arvidsson et al., 2015; Huijbregts et al., 2006; M. A. J. Huijbregts et al., 2010). The influence of this assumption, especially about electricity use in the foreground system, was examined through sensitivity analysis. Climate change is another important global environmental issue (Change, 2013). The characterization factor of climate change is expressed as Global Warming Potential (GWP). In this study, a time horizon of 100 years was investigated (Arvidsson et al., 2015; Healy et al., 2008; Kim and Fthenakis, 2013). Human toxicity and ecotoxicity include all used substances, chemicals, and their emissions that are toxic to humans and the environment (Arvidsson et al., 2014).

Water uses and climate change impact categories were investigated based on impact assessment from the ReCiPe midpoint method. The indicators are evaluated in reference units, i.e. kilograms of CO₂ equivalents (eq) per year for GWP and cubic meters (m³) for water use (Goedkoop et al., 2008). The cumulative energy demand (CED) method was used for calculating cumulative

energy demand, expressed in MJ (Frischknecht et al., 2007). Human toxicity and ecotoxicity impact categories were operationalized by the USEtox® model (Hauschild et al., 2008; Rosenbaum et al., 2008). In the USEtox® model, the unit of the characterization factor for human toxicity is cases kg⁻¹ emission and for ecotoxicity PAF m³ day kg⁻¹ emission both summarized as Comparative Toxic Unit (CTU) to stress the comparative nature of the characterization factors, through a subscript “h” and “e” to show human toxicity and ecotoxicity, respectively (M. Huijbregts et al., 2010).

2.4. Sensitivity and Statistical Analyses

Regarding production and application of immature products, uncertainty exists about their environmental impacts in early stages of technological development. “What-if” sensitivity analysis can consider how variations in different input parameters (X_1, X_2, \dots, X_n) can affect the output and result (y) (Pianosi et al., 2016). Therefore, to assess these uncertainties from a “what-if” perspective, parameters including acid ($\text{HCl} + \text{H}_2\text{SO}_4$), ammonia, ethanol, methanol, DCC, NHS, water recovery, and electricity were considered based on functional unit 1 kg Hg(II) removal for both adsorbents.

All laboratory experiments were carried out in triplicate for each condition and repeated at least twice. The Shapiro-Wilk test investigated normality distributions of data. One-way analysis of variance (ANOVA) and Duncan tests were used to compare the environmental impacts of functionalized GO-based and Fe_3O_4 -based composites for 1 kg Hg(II) removal from polluted water. A t-test was performed to determine any significant differences between the environmental impacts of MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ for 1 kg Hg removal. Analyses of mean differences between all included impact categories in the MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ were considered by the independent t test in a significant difference ($\text{sig} <$

0.05). All statistical analyses were carried out using SPSS 17.0 and Excel 2007. Significance level for all tests was set at 0.05.

3. Results and Discussion

3.1. Effect of functionalized GO and Fe₃O₄

Table 3 presents results of comparing cradle-to-use life cycle impacts of Hg(II) removal by functionalized GO-based and Fe₃O₄-based composites. In Table 3, the results of ANOVA and Duncan tests display significant differences between different stages in both adsorbents for 1 kg Hg(II) removal in all five impact categories including climate change, water use, cumulative energy demand, human toxicity, and ecotoxicity. Results showed that functionalization increases capacity adsorption for both adsorbents (see Table 1 in SI). However, for all included impact categories in both adsorbents except water use in GO-based, the functionalization increases them for 1 kg Hg(II) removal. The results suggest that the environmental impacts of both studied adsorbents increase during functionalization, despite the increase in their adsorption capacity.

Table 3

Comparison and effect of functionalizing on impact categories studied based on 1 kg Hg removal

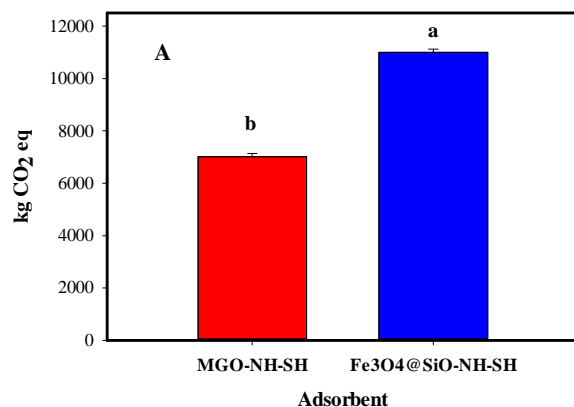
Material	Climate change kg CO ₂ eq	Water use M ³	Cumulative energy demand MJ	Human toxicity CTU _h	Ecotoxicity CTU _e
GO	5993.3 ± 278.8 ^c	47.3 ± 2.2 ^a	98896.2 ± 4602.4 ^c	9.37E-07 ± 4.35E-08 ^c	8.8 ± 0.4 ^d
MGO	7852.5 ± 273.2 ^a	37.6 ± 1.6 ^b	133998.5 ± 4662.8 ^b	9.01E-07 ± 3.14E-08 ^c	10.9 ± 0.3 ^c
MGO-NH ₂	7567.8 ± 130.0 ^a	37.1 ± 0.6 ^b	143842.8 ± 2455.2 ^a	1.15E-06 ± 1.92E-08 ^b	59.7 ± 0.9 ^b
MGO-NH-SH	7024.2 ± 120.5 ^b	36.5 ± 0.6 ^b	147837.0 ± 2543.0 ^a	1.28E-06 ± 2.19E-08 ^a	81.7 ± 1.4 ^a
Material					
Fe ₃ O ₄	1990.6 ± 67.7 ^d	11.2 ± 0.3 ^d	47663.1 ± 1619.8 ^d	1.54E-07 ± 5.26E-09 ^d	2.8 ± 0.0 ^d
Fe ₃ O ₄ @SiO ₂	2486.9 ± 119.6 ^c	20.1 ± 0.9 ^c	60235.9 ± 2858.9 ^c	1.89E-07 ± 9.25E-09 ^c	4.0 ± 0.1 ^c
Fe ₃ O ₄ @SiO-NH ₂	8741.6 ± 251.5 ^b	38.5 ± 1.1 ^b	167047.7 ± 4810.3 ^b	8.37E-07 ± 2.40E-08 ^b	11.1 ± 0.3 ^b
Fe ₃ O ₄ @SiO-NH-SH	11007.2 ± 113.2 ^a	56.1 ± 0.5 ^a	243784.1 ± 2433.7 ^a	1.83E-06 ± 1.88E-08 ^a	109.9 ± 1.0 ^a

NOTE: Different letters (e.g. a, b, c, and d) indicate significant differences between different stages and similar letters (e.g. a and a) indicate non-significant differences between different stages at $P \leq 0.05$ as determined by

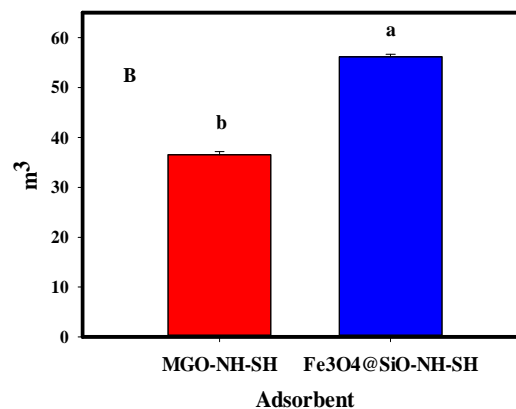
ANOVA followed by a multiple range test (Duncan). The decrease of values for the applied abbreviations (e.g. a, b, c, and d) are followed as: a>b>c>d.

3.2. Comparison between MGO-NH-SH and Fe₃O₄@SiO-NH-SH

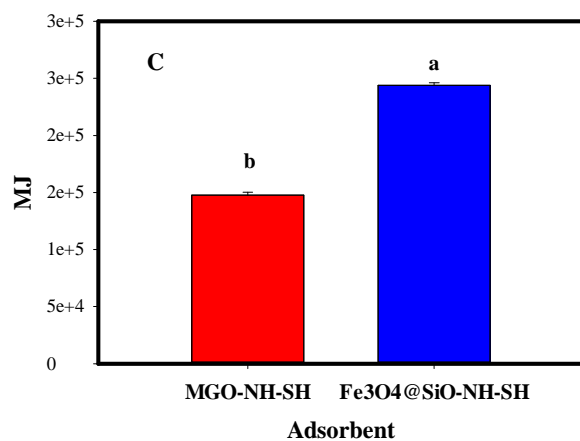
Fig. 2 depicts the results of t-test comparing the cradle-to-use life cycle impacts of studied impact categories for 1 kg Hg removal between MGO-NH-SH and Fe₃O₄@SiO-NH-SH. The results indicated that the average values of climate change, water use, cumulative energy demand, human toxicity, and ecotoxicity in MGO-NH-SH and Fe₃O₄@SiO-NH-SH were in the ranges of 7024.2 and 11007.2 kg CO₂ eq, 36.5 and 56.1 M³, 147837.0 and 243784.1, 1.28E-06 and 1.83E-06 CTU_h, and 81.7 and 109.9 CTU_e, respectively. In total, Fe₃O₄@SiO-NH-SH is higher in all five impact categories than MGO-NH-SH for 1 kg Hg removal; approximately 37, 34, 40, 31, and 26% more climate change, water use, cumulative energy demand, human toxicity, and ecotoxicity, respectively. All results of impact categories indicated that MGO-NH-SH is more environmentally friendly adsorbent than Fe₃O₄@SiO-NH-SH for 1 kg Hg(II) removal.



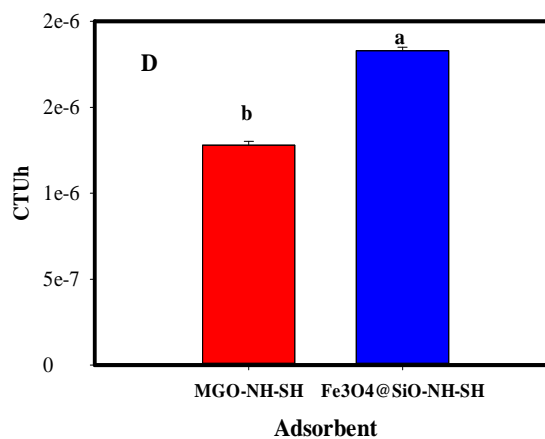
A: Climate change potential



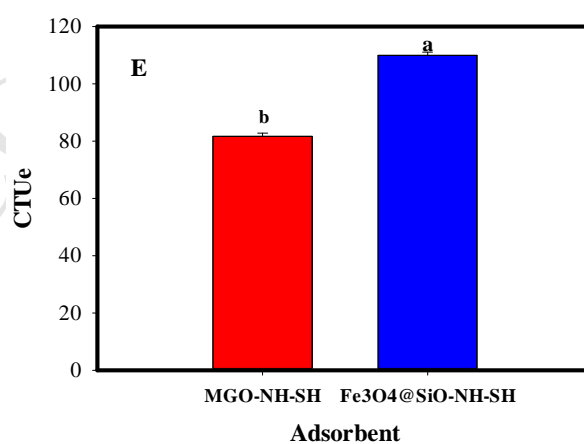
B: Water use



C: Cumulative energy demand



D: Human toxicity



E: Ecotoxicity

Fig. 2. Comparison of studied impact categories for 1 kg Hg removal between MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$; A: Climate change potential, B: Water use, C: Cumulative energy demand, D: Human toxicity, and E: Ecotoxicity.

According to Figs 3 and 4, the results for climate change potential are similar for both adsorbents. Based on these results, the main factors affecting climate change potential for MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ are use of electricity for heating and cooling (58 and 71%) in the synthesis process, similarly to that described in the study of Pini et al., (Pini et al., 2015) and the input of chemical ethanol for washing (21 and 18.5%) in the production stage. Additionally, DCM as a solvent in functionalization with an amine group (EDA) contributes with 12% to the climate change in MGO-NH-SH. The contributions of other materials for both adsorbents in total are less than 10%. Therefore, a reduction of ethanol, DCM, and energy used can decrease climate change significantly. These scenarios are tested in sensitivity analysis.

Regarding water use for both adsorbents, the use of ethanol for washing during the production stage of both adsorbents is the main use of water, chiefly owing to water use in the production of ethylene and subsequently ethanol. Electricity production is the next contributor to water use. Figs 3 and 4 show that using toluene in $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ production and DCC in production of both adsorbents has a significant impact on water use for adsorbents. The effect of electricity decrease, ethanol, toluene, water, and DCC recovery are further investigated in the sensitivity analysis scenarios.

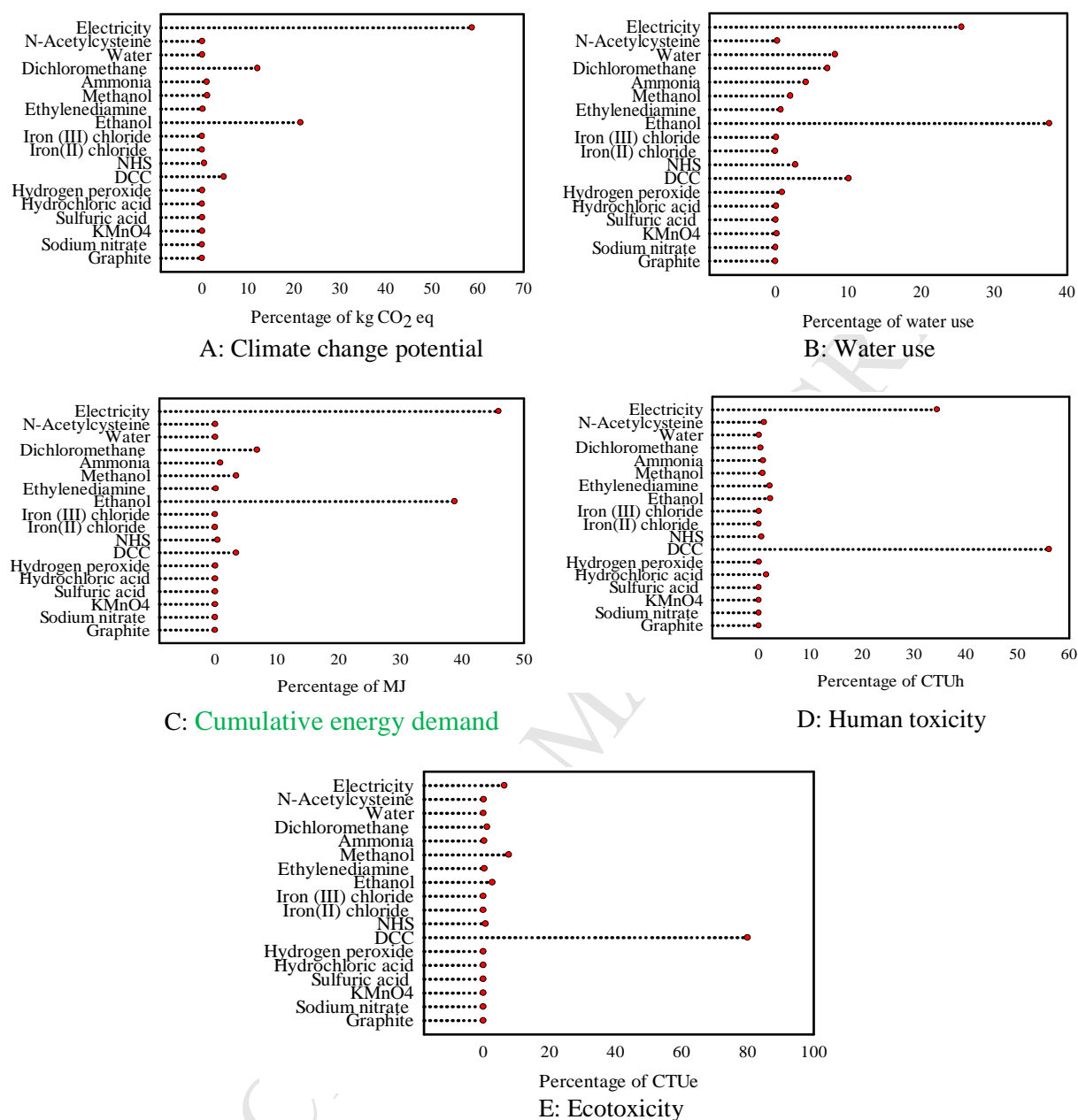
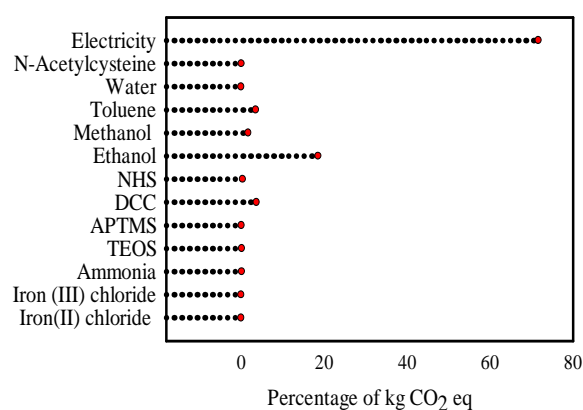


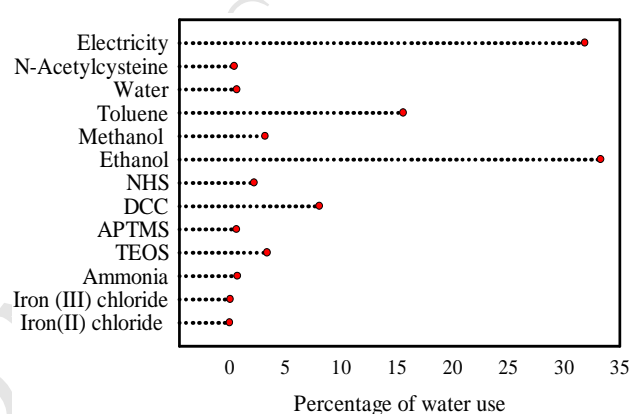
Fig. 3. The results of all impact categories separately for MGO-NH-SH based on 1 kg Hg removal; A: Climate change potential, B: Water use, C: Cumulative energy demand, D: Human toxicity, and E: Ecotoxicity. NOTE: the length of the dotted line show effect of every input on different impact categories.

The results of cumulative energy demand for both adsorbents are similar to those of the climate change potential. Cumulative energy demand (approximately 50%) is the use of electricity (for heating, cooling, and sonication) in the production stage. Producing chemical ethanol as a

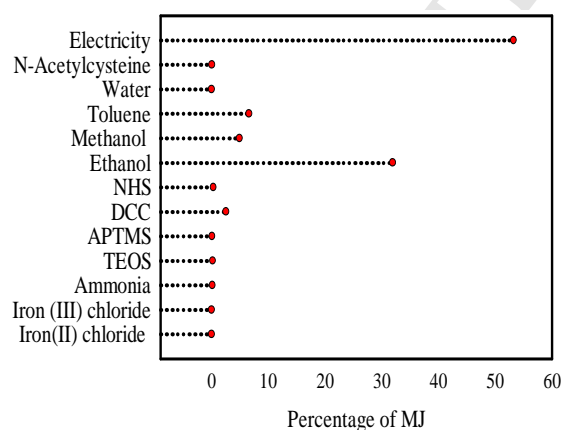
solvent for washing in the production stage of MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH-SH}$ contributes with 39 and 32% of the cumulative energy demand, respectively. The effects of other materials are less than 15% in total. Consumption of energy is so different on laboratory and industrial scales that a 95% decline in electricity consumption was investigated as a scenario in the sensitivity analysis. The results of study Gavankar et al. (2015) on scaled-up of carbon nanotube production showed that scaling up and production volume could reduce 84% to 94% of its cradle-to-gate impacts.



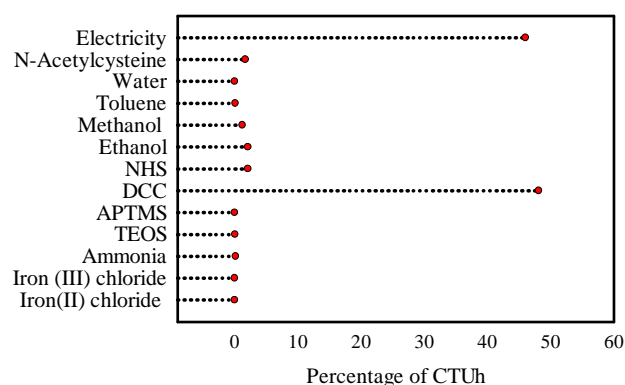
A: Climate change potential



B: Water use



C: Cumulative energy demand



D: Human toxicity

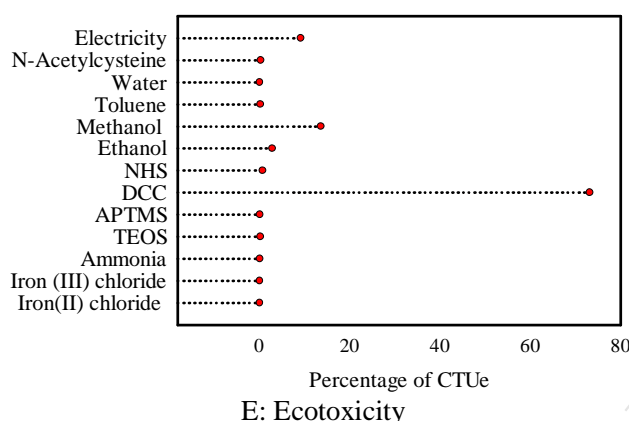


Fig. 4. The results of each impact category for $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ based on 1 kg Hg removal; A: Climate change potential, B: Water use, C: Cumulative energy demand, D: Human toxicity, and E: Ecotoxicity. NOTE: the length of the dotted line show effect of every input on different impact categories.

The main contributor to human toxicity and ecotoxicity has been the use of DCC as a coupling reagent in the production of both adsorbents. In human toxicity, the main contributor is pyridine, used in production of cyclohexyl isocyanide and, subsequently, DCC in the production of both adsorbents. Electricity use also has a high effect on human toxicity for studied adsorbents. In ecotoxicity, the main contributor is the use of rhodium in the production of cyclohexylamine and then of using cyclohexylamine in the production of N-cyclohexyl formamide, and as well as using pyridine in the production of cyclohexyl isocyanide and subsequently DCC for production of both adsorbents. (See DCC production in SI) After DCC, the use of methanol in the thiol-functionalization stage has higher impact than other inputs on ecotoxicity. The potential effect of reducing these highly-used materials and energy as a results of scale-up, is investigated in scenarios including DCC and methanol recovery, and electricity reduction in the sensitivity analysis.

3.3. Sensitivity analysis

Adsorbents, specifically nanoadsorbents, play an important role in water and wastewater treatment, and their production is still primarily at laboratory scale (Cui et al., 2015b; W. Zhang et al., 2013). Clearly, laboratory scale and industrial scale differ, particularly in term of LC (Arvidsson et al., 2015; Gavankar et al., 2015; Kim and Fthenakis, 2013). Hence, sensitivity analysis can be important in assessing uncertainty in environmental impacts for scale-up production. Furthermore, understanding the main contributing processes in industrial-scale production can reduce the number of unknown environmental impacts (Arvidsson et al., 2014). The parameters investigated in sensitivity analysis for MGO-NH-SH included recovery of water used for washing in the production stage and reduction of electricity use (0–95%), and as well acid ($\text{HCl} + \text{H}_2\text{SO}_4$), ammonia, ethanol, methanol, DCC, and NHS recovery (0–90%). For $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$, the parameters included water recovery and reduction of electricity use (0–95%) and ammonia, ethanol, methanol, toluene, DCC and NHS recovery (0–90%), see the Fig. 5 and 6, and Table S.7 and S.8.

As the results of sensitivity analysis in Figs 5 and 6 show, recovery of water directly used as a washing agent during the productions process of both adsorbents does not create a considerable change in the studied impact categories; only a small change (almost 7%) was calculated in the water use impact category of MGO-NH-SH.

As expressed above, due to the difference between electricity used in the laboratory and on an industrial scale (Kim and Overcash, 2003), the baseline scenario's reduction of electricity use by 95% reduces all impact categories between 30 to 50%, except ecotoxicity (less than 8%). The slight decrease in ecotoxicity is mostly due to lower emissions of phenol during production of electricity in fossil fuel power plants. This result suggests that the decrease in electricity used by fossil fuel power plants can reduce all studied impact categories on an industrial scale; clearly,

using green electricity in industry may reduce all included impact categories in this study, as well as those not included.

Recovery of 90% of the acids used in the graphite oxidation process via the Hummer method for MGO-NH-SH production showed that all five impact categories studied scarcely ever change (Fig. 5). However, the study of Arvidsson et al. (2014) on LCA of 1 kg graphite oxide production by the Hummer method demonstrated that 90% acid recovery reduces water use by almost two-thirds. But, consistent with our study, they saw no significant change on other impacts (cumulative energy demand, human and eco toxicity) (Arvidsson et al., 2014). The difference in water use between this study and theirs may be caused by less use of acid in the production of MGO-NH-SH due to difference between functional unit of this study '1 kg Hg removal' and theirs '1 kg graphite oxide production'. Acid recovery is very important on an industrial scale, because it can positively affect many other environmental impacts (Arvidsson et al., 2014; Uihlein and Schebek, 2009). Recovery of ammonia that as a precipitating agent in co-precipitation method in magnetization of adsorbents play a vital role, is important as well. Hence, while 90% recovery was investigated for both adsorbents, all five impact categories scarcely changed; only a minor change was observed, of almost 4% less water use for MGO-NH-SH than for the baseline (Figs. 5 and 6).

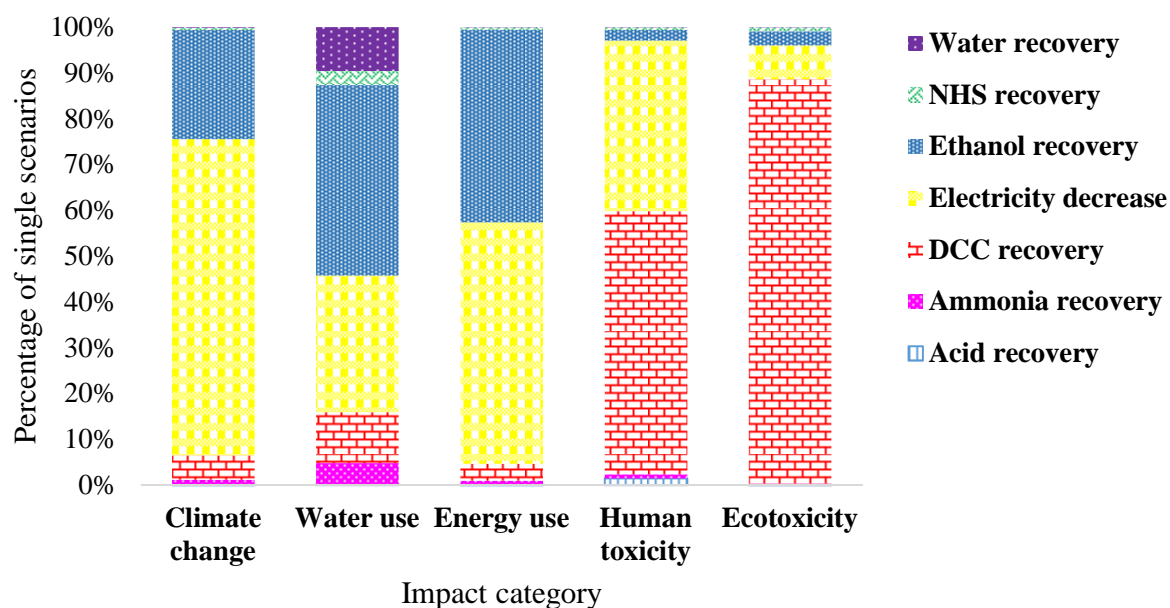


Fig. 5. The results of the sensitivity analysis for MGO-NH-SH, showing the importance of the single scenarios for the reduction of each impact category in percentage

As Figs. 5 and 6 show, DCC recovery reduced climate change, water use, and cumulative energy demand by almost 3 to 10% for both adsorbents. The largest reduction was attributed to human toxicity and ecotoxicity, roughly 50 and 70% for both studied adsorbents, respectively. As mentioned in the previous section, changing from 90% recovery of DCC and baseline of human toxicity and ecotoxicity in both adsorbents is mostly the result of emissions of pyridine and rhodium during process of DCC production. Therefore, DCC recovery can significantly affect the reduction of human toxicity and ecotoxicity on an industrial scale. The recovery of NHS as another coupling reagent in the production of both adsorbents scarcely ever changed any of the studied impact categories.

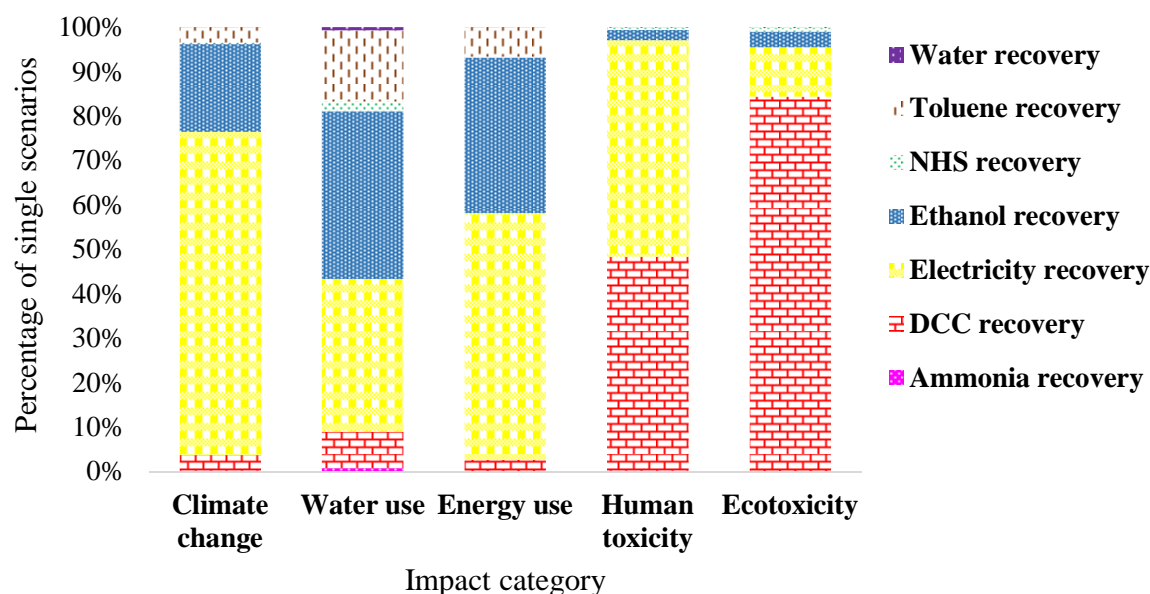


Fig. 6. The results of the sensitivity analysis for $\text{Fe}_3\text{O}_4@\text{SiO}-\text{NH}-\text{SH}$, showing the importance of the single scenarios for the reduction of each impact category in percentage

Ethanol recovery during the production process of both adsorbents reduced climate change almost 20%, water and cumulative energy demand almost 30%, and less than 3% for human toxicity and ecotoxicity. These increases in climate change, water, and cumulative energy demand impact categories in the baseline by greater than 90% ethanol recovery are mostly due to use of water and energy in production of ethylene and then hydration of ethylene to ethanol. These results demonstrate that chemical ethanol recovery is useful and important for reduction of environmental impacts in industrial scale production of these adsorbents.

4. Conclusion

This study developed an environmental assessment of nanoadsorbents as a special application of nanoproducts. The results demonstrate that functionalization of both studied nanoadsorbents in

order to increase their adsorption capacity cause a large increase in their environmental impacts and may differ for other nanoadsorbent products.

Fig. 2, with the results of all included impact categories for both studied nanoadsorbents (MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$, suggest that MGO-NH-SH has a lower environmental impact in all included impact categories compared to $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ for 1 kg Hg removal. Furthermore, in a prospective approach, finding factors that perform as the main contributors in all five impact categories for both nanoadsorbents is advisable. For example, Arvidsson et al. (2014) showed that the hydrazine and diethyl ether used in graphene production by chemical reduction and ultrasonication, respectively, are strong contributors in all studied impact categories. In this study, electricity used for heating and cooling and chemical ethanol used in washing in production are the main contributors in cumulative energy demand, water use, and climate change. Similarly, DCC plays an important role in human toxicity and ecotoxicity. In industrial production of these nanoadsorbents, material recovery can play a big role in reducing impacts in all included impact categories, but it is important to know where efforts to recover has the largest effect. For example, the recovery of 90% of DCC in the production stage of MGO-NH-SH and $\text{Fe}_3\text{O}_4@\text{SiO-NH-SH}$ reduces human toxicity and ecotoxicity by about 50 and 70%, respectively, whereas the NHC recovery had no visible effect in any impact category.

Overall, these results lead to a generalized finding, that the production of nanomaterials, particularly in specialized applications, e.g. nanoadsorbents, can be optimized through performing an assessment of the environmental impacts of their production and use at an early stage of technological development, which assist in understanding of their thought environmental impacts.

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